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The Electrochemical and Thermal Stability of PEDOT-based Composite Films

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*The electrically conductive composite films based on poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized. The PEDOT/silicate composite was prepared by the **in-situ** oxidative polymerization of EDOT monomer using ferric toluene sulfonate (FTS) oxidant in which tetraethylorthosilicate was added to form inorganic silicate network by sol-gel transformation. The PEDOT-gold composite film was also prepared by the **in-situ** redox reaction between PEDOT in neutral state and $AuCl_3$. The neutral PEDOT was oxidized by $AuCl_3$ while $AuCl_3$ was reduced to form Au metal. These PEDOT based composite films were repeatedly oxidized and reduced and the electrochemical and thermal stability was monitored by cyclic voltammetry. PEDOT-gold film exhibited highly enhanced electrochemical as well as thermal stability compared to PEDOT-PSS and PEDOT-silicate films.*

Keywords: electrical stability; gold; *in-situ* redox system; PEDOT

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) has a number of attractive properties that make them suitable for many applications such as polymer light emitting diodes (PLEDs), capacity etc. [1–3]. In the

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preparation of PLEDs, PEDOT has been used as a buffer layer between ITO and light emitting layer for balancing electron and hole current. PEDOT is a stable conjugated polymer with high transparency and high electrical conductivity in the doped (oxidized) state. However, recent reports appearing in the literature indicate that degradation of PLEDs devices may be at least partially due to a degradation of the PEDOT [4]. In this regards, the stability of conjugated organic materials under electron transport is of great importance for the lifetime of PLED devices. The degradation process involves the migration and accumulation of sulfur compounds resulting from the degradation of PEDOT at the cathode interface [5].

Here, we have synthesized the PEDOT-based composite films for expecting enhanced electrochemical stability. PEDOT/gold composite film was synthesized by the *in-situ* redox reaction between PEDOT in neutral state and $AuCl_3$. For the comparison of the electrochemical stability of PEDOT-gold film, PEDOT:poly(styrene sulfonic acid) (PSS) (Baytron P) and PEDOT/silicate film were also synthesized. These films were repeatedly oxidized and reduced and the current changes during redox cycle were monitored by cyclic voltammetry. These films were also situated at elevated temperature and the variation of electrical conductivity was monitored. With these experiments, the influence of the electrochemical and thermal treatments on the stability of the polymer film was investigated.

EXPERIMENTAL SECTION

Material

3,4-ethylenedioxythiophene (EDOT) was offered by Aldrich and was distilled and stored in a refrigerator. Tetraethylorthosilicate (TEOS) and nitromethane (NM) from Aldrich, 3-mercaptopropyl-trimethoxysilane (MPS) from Sigma, PEDOT:PSS (Baytron P® AI 4083) and 40 wt.% ferrictoluenesulfonate (FTS) in n-butanol solution from Bayer AG, and gold(III) chloride from Kojima Chemicals were used as received.

Synthesis of PEDOT/Silicate Film on the ITO Glass

In order to provide mechanical strength and adhesion between substrate and PEDOT film, inorganic silicate was incorporated by *in-situ* sol-gel process. The preparation of PEDOT/silicate composite films was carried out according to the procedure described by M. Lee *et al*. [6].

Preparation of PEDOT/Gold Composite Film

The PEDOT/gold composite film was also prepared by the *in-situ* redox reaction between PEDOT in neutral state and $AuCl_3$. The preparation of PEDOT/gold composite films was carried out according to the procedure described by M. Lee *et al*. [6].

Fabrication of PEDOT:PSS (Baytron P) Film

PEDOT:PSS solution was coated onto ITO by spin-casting. The films were heated to 100°C.

Electrical and Thermal Treatment

The three different PEDOT-based composite films were transferred in an electrochemical cell containing an acetonitrile solution of 0.1 M $LiClO_4$. The PEDOT based composite films coated on ITO as anodes, platinum plates as counter electrodes and Ag/AgCl (sat'd KCl) as reference electrode were used respectively. Repeated galvanic pulses was impressed between −1.0 and 1.0 V with the same duration (25 ms) using a Parstat 2263 in a three-electrode cell, where reversible doping/dedoping process of polymer films is maintained.

In order to examine the thermal stability, the films were placed in convection oven at 200°C for 24 h.

Instrument-Analysis

Cycle voltammetry (CV) was studied by cyclic scanning of the potential between −1.0 and 1.0 V with the sweep rate of 50 mV/s in the same electrode. Surface resistance measurements were carried out by means of the four-probe technique using a Keithley 236 current source and Keithley 617 electrometer.

RESULTS AND DISCUSSION

We prepared the three different PEDOT-based composite films: PEDOT:PSS, PEDOT/silicate, PEDOT/gold. The influence of the electrochemical and thermal treatments on the stability of the polymer films was investigated.

During the repeated galvanic pulse at −1 and 1 V, cyclic voltammograms between −1 and 1 V (three electrode system, scan rate 50 mV/s) were recorded for the three different films. As shown in Figure 1(a), in the PEDOT:PSS film, a main anodic peak centered at 300 ~ 350 nm

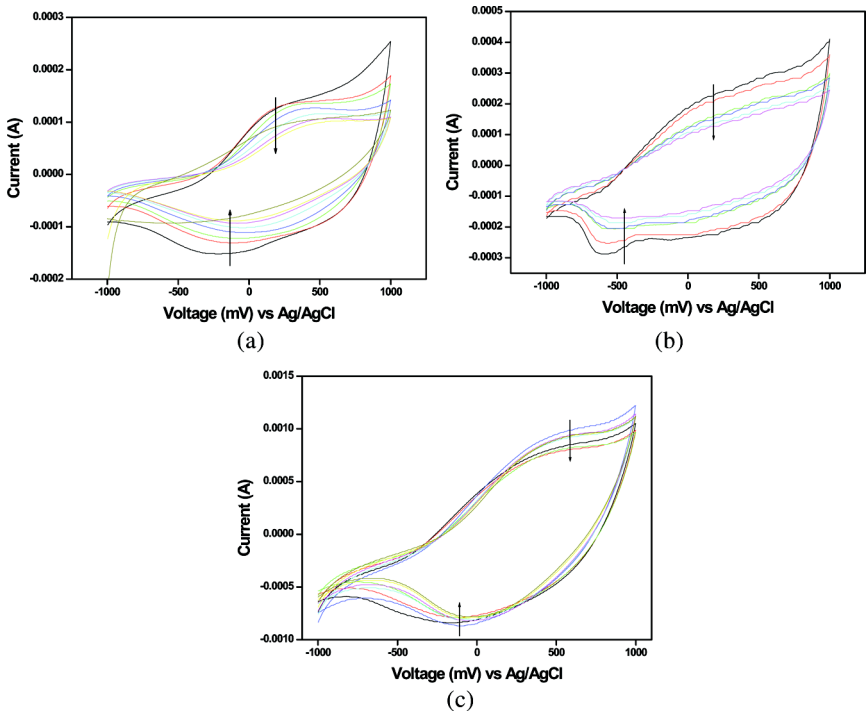

FIGURE 1 Cycle voltammograms of PEDOT:PSS (a), PEDOT/silicate (b), PEDOT/gold (c) in between −1 and +1 V. Scan rate: 50 mV/s.

and cathodic peak at −155 ∼ −100 nm is observed. The PEDOT/silicate film is oxidized and reduced resulting in a broad peak at 350 ∼ 500 nm and at −500 ∼ −550 nm, respectively as shown in Figure 1(b). In the same manner, the PEDOT/gold film is oxidized and reduced showing an anodic peak centered at 450 ∼500 nm and one well-defined reduction peak at −20 ∼ −50 nm as shown in Figure 1. As the number of impressed redox pulse is increased, the redox peak current decreased gradually, which means some degradation process occurs. The PEDOT/gold films displayed distinct oxidation and reduction peaks, and the electrochemical stability is highly satisfactory compared to the PEDOT:PSS and PEDOT/silicate film. Figure 2 showed the degradation of electrochemical activity for the three different PEDOT-based composite films for 108,000 cycles. It was calculated from the relative current decrease ratio (%) I/I_0 where I is current at reduction peak: at −1.35 V for PEDOT:PSS;

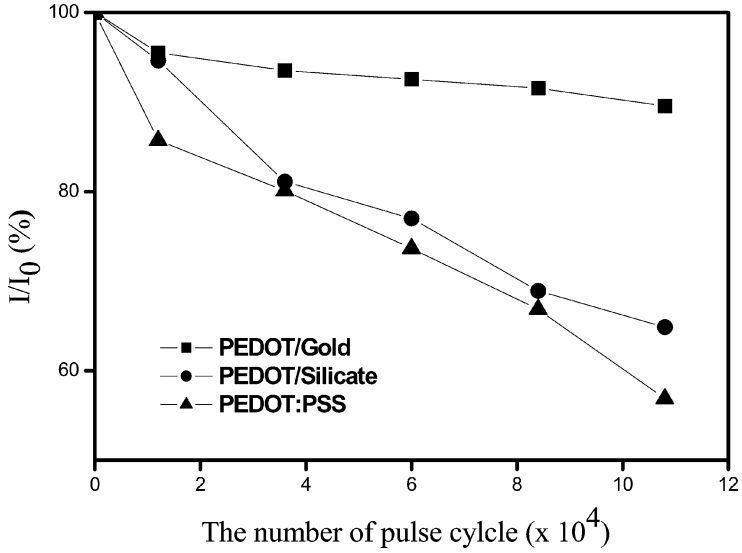

FIGURE 2 Relative electrochemical activity of polymer films: relative current ratio (%), I_i/I, where I_i is initial current.

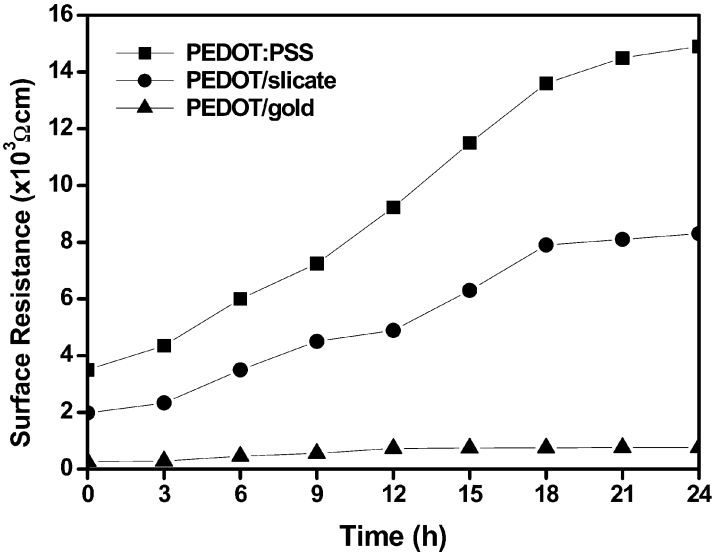

FIGURE 3 Surface resistance of PEDOT:PSS, PEDOT/silicate, and PEDOT/gold film thermal treated at 200°C as an function of time.

at $-5.46\,V$ for PEDOT/silicate; at $-1.26\,V$ for PEDOT/gold, and I_0 is initial current. The electrochemical activity of PEDOT/gold film was slowly decreased up to 10.46%. However, in the case of the PEDOT:PSS and PEDOT/silicate film, it was considerably decreased to 43.16 and 35.16%, respectively.

Figure 3 showed conductivity decrease data upon heat treatment. The films were heated in convection oven at 200°C for 24 h [7]. Surface resistance of thermal treated PEDOT:PSS, PEDOT/silicate, and PEDOT/gold film was measured as a function of the time. The PEDOT/gold film shows highly enhanced thermal stability in which no change in surface resistance was observed after 24 h at 200°C. The increase in resistance was only 2.8% for 24 h. The surface resistance of PEDOT:PSS film and PEDOT:silicate film was increased from 3.5 to $14.9 \times 10^3\,\Omega \cdot cm$ and $1.98 \sim 8.3 \times 10^3\,\Omega \cdot cm$ over about 18 h, respectively. In this experiment, the PEDOT/gold films exhibited highly enhanced thermal and electrochemical stability compared to the PEDOT:PSS and PEDOT/silicate film.

CONCLUSION

We prepared the three different films: PEDOT:PSS, PEDOT/silicate, PEDOT/gold. The influence of the electrochemical and thermal treatments on the stability of the polymer films was investigated. The PEDOT/gold films displayed distinct oxidation and reduction peaks in cyclic voltammograms, and the electrochemical stability upon repeated redox cycle is highly enhanced compared to the PEDOT:PSS and PEDOT/silicate film. After thermal treatment at 200°C the surface resistance of PEDOT/gold film was changed only 2.8%.

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